PB90-126582

Determination, Fate, and Potential Significance of PCBs (Polychlorinated biphenyls) in Fish and Sediment Samples with Emphasis on Selected AHH-Inducing Congeners

(U.S.) Environmental Research Lab., Narragansett, RI

1988

U.S. Department of Commerce
National Technical Information Service
NTIS

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. RE
EPA/600/J-88/443		PB90-126582

4. TITLE AND SUBTITLE	5. REPORT DATE
DETERMINATION, FATE, AND POTENTIAL SIGNIFICANCE OF PCBs IN FISH AND SEDIMENT SAMPLES WITH EMPHASIS ON SELECTED AHH-INDUCING CONGENERS	accepted 1988
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S)	8. PERFORMING ORGANIZATION REPORT NO.
J. A. Huckins , T.R. Schwartz , J.D. Petty , L.M. Smith	ERLN-N098
9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT NO.
US Fish and Wildlife Service National Fisheries Contaminant Research Center Route 1, Columbia, Mo. 65201	11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS	13. TYPE OF REPORT AND PERIOD COVERED
US EPA, Environmental Research Laboratory South Ferry Road Narragansett, R.I. 02882-1198	Journal article
	14. SPONSORING AGENCY CODE EPA/600/05

15. SUPPLEMENTARY NOTES

Chemosphere, Vol. 17, No. 10, pp. 1995-2016 (1988)

16. ABSTRACT

Total PCB residues, non-o,o'-Cl PCBs, and the most AHH-active mono-o,o'-Cl PCB congener were determined in Great Lakes fish and sediment samples. Toxic 3,3',4,4'-tetrachlorobiphenyl and 2,3,3',4,4'-pentachlorobiphenyl were detected in both fish and sediments. There appeared to be some reduction in the percentage content of the selected AHH-active congeners in fish and sediment PCB residues when compared to their percentage content in the Aroclor mixtures suspected as sources of contamination. The TCDD equivalents (AHH induction potency normalized to TCDD, times residue concentration in pg/g) were as high as 666 pg/g in fish; PCB residues in one sediment sample appeared to have undergone reductive dechlorination by anaerobic microorganisms.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
PCB Great Lakes fish PCB residue sediment PCB residue aroclors		

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES
RELEASE TO PUBLIC	UNCLASSIFIED	25
	20. SECURITY CLASS *(This page)*	22. PRICE
	UNCLASSIFIED	

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

REPRODUCED BY
U.S. DEPARTMENT OF COMMERCE
NATIONAL TECHNICAL INFORMATION SERVICE
SPRINGFIELD, VA. 22161

Chemosphere, Vol.17, No.10, pp 1995-2016, 1988
Printed in Great Britain

EPA/600/J-88/443
0045-6535/88 $3.00 + .00
Pergamon Press plc

DETERMINATION, FATE, AND POTENTIAL SIGNIFICANCE OF PCBs IN FISH AND SEDIMENT SAMPLES WITH EMPHASIS ON SELECTED AHH-INDUCING CONGENERS

James N. Huckins*, Ted R. Schwartz

US Fish and Wildlife Service
National Fisheries Contaminant Research Center
Route 1, Columbia, MO 65201

Jimmie D. Petty

US EPA-EMSL/LV, Office of R. & D./ORD
P. O. Box 93478, Las Vegas, NV 89193-3478

Lawrence M. Smith

US EPA, Hatfield Marine Science Center
Newport, OR 97365

*Corresponding author

ABSTRACT

Total PCB residues, non-o,o'-Cl PCBs, and the most AHH-active mono-o,o'-Cl PCB congener were determined in Great Lakes fish and sediment samples. Toxic 3,3',4,4'-tetrachlorobiphenyl and 2,3,3',4,4'-pentachlorobiphenyl were detected in both fish and sediments. There appeared to be some reduction in the percentage content of the selected AHH-active congeners in fish and sediment PCB residues when compared to their percentage content in the Aroclor mixtures suspected as sources of contamination. The TCDD equivalents (AHH induction potency normalized to TCDD, times residue concentration in pg/g) were as high as 666 pg/g in fish; PCB residues in one sediment sample appeared to have undergone reductive dechlorination by anaerobic microorganisms.

INTRODUCTION

Polychlorinated biphenyls (PCBs) are a class of synthetic chlorinated compounds with the chlorines attached in one or more of 10 positions resulting in 209 theoretically possible structural congeners, although the number of congeners observed in technical formulations is much smaller (1,2). Most PCB isomers in the U.S. originated from one of several products designated as Aroclors^{R}. The different Aroclors have capillary gas chromatographic (GC) profiles of approximately 100 components (3), however many of these co-elute when using packed column GC analysis. The advent of high resolution PCB analysis has enabled separation of 187 of the 209 potential PCB congeners (4).

Concern about the occurrence of PCBs in the environment centers on their persistence, bioaccumulation, and toxicity (5). Certain congeners (primarily those having none or one

NTIS is authorized to reproduce and sell this report. Permission for further reproduction must be obtained from the copyright owner.

chlorine substituted in the ortho, ortho'-positions [o,o'] of the phenyl rings and one or more meta- and para-Cls on each ring) are particularly toxic and are potent inducers of liver microsomal aryl hydrocarbon hydroxylase (AHH) (6-8). These coplanar non-o,o'-Cl congeners are approximate isosteremers of 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD). Their ability to induce mixed function oxidase activity is similar to that observed from exposures to TCDD (9). The ethoxyresorufin O-deethylase (EROD) and AHH induction potency of 3,3',4,4',5-pentachlorobiphenyl (PeCB, IUPAC 126) is one-fourth to one-third that of TCDD (10). Several studies of in vitro AHH/EROD induction and binding of halogenated aromatic compounds have confirmed the direct relationship between their induction potency and toxicity to mammals (6,11-13). Recently, Kubiak et al. (7) Smith et al. (14) and Kannen et al. (15) reported the relative AHH induction potencies of several non-o,o'-Cl and mono-o,o'-Cl PCBs. In two of these studies (7,14) the AHH induction potency of each congener was normalized against TCDD and multiplied by its respective concentration in the eggs of the piscivorous Forster's tern (Sterna forsteri) yielding "TCDD equivalents." Although TCDD concentration was elevated in the eggs (22 and 52 pg/g in two samples), it accounted for only 2% of the total AHH enzyme induction potential of the sample residues (14). Since mono-o,o'-Cl and non-o,o'-Cl PCBs represented 98% of the AHH induction potential in the egg samples (assuming an additive response), their presence in environmental food chains is a major toxicological concern. In the tern eggs 2,3,3',4,4'-PeCB (IUPAC 105) and 3,3',4,4'5-PeCB appeared to account for most of the TCDD-like activity.

Mayer et al. (16) examined the toxicity of Aroclors 1242, 1248, 1254 and 1260 to rainbow trout (Salmo gairdneri), bluegill (Lepomis macrochirus) and channel catfish (Ictalurus punctatus), and found that Aroclor 1248 was the most toxic mixture, closely followed by Aroclor 1242. Stalling et al. (17) compared the toxicity of non-o,o'-Cl 3,3',4,4'-tetrachlorobiphenyl (TCB, IUPAC 77) to mono- through four-o,o'-Cl congener fractions of Aroclor 1248 in a 50-day flow-through rainbow trout exposure, and found that the toxicity of 3,3',4,4'-TCB was at least 40 times that of o,o'-Cl substituted fractions.

Analysis of non-o,o'-Cl PCBs in Aroclor mixtures by Huckins et al. (18) revealed that Aroclor 1248 contained the largest amount of non-o,o'-Cl congeners with four or more chlorines (3400 µg/g 3,3',4,4'-TCB plus < 250 µg/g 3,3',4,4',5-PeCB). Aroclor 1242 contained the second-largest amount of non-o,o'-Cl congeners (2400 µg/g 3,3',4,4'-TCB plus < 250 µg/g 3,3',4,4',5-PeCB). Although 3,3',4,4',5-PeCB in Aroclor mixtures could not be precisely quantified, it was highest in Aroclor 1248 followed by 1242 and 1254, respectively. The recent and comprehensive works of Kannan et al. (19,20) found the same trend for 3,3',4,4'-TCB content in Aroclors but 3,3',4,4'5-PeCB was higher in Aroclor 1254 than in Aroclor 1242. The relative concentrations of 3,3',4,4'-TCB in Aroclors are consistent with the fish toxicity reported for Aroclor mixtures (16).

Investigators have detected non-o,o'Cl PCBs in eggs of Forster's terns from Lake Michigan (7), in marine mammals and humans (21), and composite fish samples from the Hudson (22) and Ohio Rivers (18). A number of non-o,o'-Cl PCBs (3,3',4,4'-TCB, 3,3',4,4'5-PeCB, 3,3',4,4',5,5'- hexaclorobiphenyl) and 2,3,3',4,4'-PeCB were detected by GC-mass spectrometry (MS) in the eggs, whereas only 3,3',4,4'-TCB was detected in fish samples with a GC-electron capture detector (ECD).

To assess residue levels of non- and mono-o,o'Cl-substituted PCBs in Aroclors and environmental samples, a comprehensive analytical method is needed to isolate and quantify these toxic congeners. Non-o,o'-Cl PCBs have been separated from Aroclor mixtures by using columns of activated carbon dispersed on polyurethane foam (18). The isolation of small amounts of non-o,o'-Cl congeners from technical PCB mixtures was based on the high specificity of activated carbon to adsorb chlorinated coplanar aromatics (17). The elution volumes of PCB congeners from carbon increased with decreasing o,o'-Cl substitution and increasing degree of chlorination in the meta and para ring positions (17). More recently, improvements have been made in carbon chromatography used for these separations (19,20,23) and in the congener-specific capillary gas chromatographic analysis of PCBs (4). The methods reported herein incorporate some of these improvements.

Differences in physicochemical properties between o,o'-Cl and non-o,o'-Cl substituted PCB congeners suggest that dissimilarities in environmental fate may be observed. In particular, non-o,o'-Cl PCBs appear to have lower vapor pressures, higher melting points, and greater adsorption on active and deactivated organic surfaces than do other PCB isomers (17,24,25). In this work we examined selected environmental fish and sediment samples for the mono-o,o'-Cl 2,3,3',4,4'-PeCB and three non-o,o'-Cl PCB congeners and discuss their potential fate and environmental significance.

EXPERIMENTAL

Sample Description and Origins: The fish and sediment samples were obtained from the U.S. Environmental Protection Agency Central Regional Laboratory in Chicago, IL and were collected in August 1978. A specific description of sampling method and location was not provided; however, all samples were from Waukegan Harbor, IL. Sediment samples were received frozen and were from locations designated as "Slip 3" or "Upper Harbor." Selected sediment samples were analyzed for organic carbon content with a CO_2 Coulometer (Coulometrics Inc., Wheat Ridge, CO). Organic carbon content for three of the five sediment samples (S422, S423 and S425) were 8.2 ± 2.7%, 8.2 ± 0.5% and 3.7 ± 0.7%, respectively. Samples S421 and S424 were not analyzed for organic carbon because of the extremely high PCB content of and the hazards associated with PCB combustion products. Frozen fish samples (Table 1) were received homogenized and were stored at minus 25°C until analysis.

Method: Sediment samples were thawed at room temperature and placed into a hexane-rinsed foil pan and air dried for five days. The sediment was broken up and homogenized with a stirring rod and 30 to 52 g portions were mixed with anhydrous sodium sulfate until dry for column extraction. Fish tissue subsamples of 10.0 g (except F142 which was 6.9 g) were thawed, mixed, and dried with sodium sulfate and placed into glass extraction columns. Fish and sediment samples were separately extracted with 200 mL of methylene chloride. Methylene chloride was evaporated from an aliquot of each fish extract and lipid was determined gravimetrically. Gel permeation chromatography (GPC) was used for removal of lipid from fish sample extracts (26). PCB residues were enriched by adsorption column chromatography on silica gel and sulfuric acid silica gel (27). Prior to GC analysis, nitric acid rinsed copper wool (approximately 1 g) was added to the sediment extracts to remove elemental sulfur. Additional details of these enrichment procedures have been published (28,29).

Table 1. Description of fish samples analyzed

Sample Designation	Sample Type\1	Percent Lipid	Fish Species
F141	WBC (n=6)	3	Ictalurus melas black bullhead
F142	Offal (n=1)	1	Micropterus salmoides largemouth bass
F143	WBC (n=3)	2	Poxomis nigromaculatus black crappie
F144	WBC (n=6)	10	Catostomus commersoni white sucker
F145	WB (n=1)	5	Oncorhynchus kisutch coho salmon
F146	WB (n=1)	1	Poxomis annularis white crappie
F147	WBC (n=5)	7	Perca flavescens yellow perch

\1 WB = whole body; WBC = whole body composite

The elution scheme reported by Smith (29) was modified to recover non-o,o'-Cl PCBs. An aliquot of the PCB residues, isolated from the sample extracts after the cleanup with sulfuric acid-silica gel and silica gel, was diluted in 30 mL of 1:1 methylene chloride:cyclohexane. This solution was then applied to 50 mg of carbon dispersed with glass fibers in a 1-cm i.d. column as described by Smith (23). Nitrogen gas at 2-3 psi was used to maintain solvent flow at 3 mL/min.

The bulk of the o,o'-Cl substituted PCB components were eliminated by eluting the column with 40 mL of 1:1 methylene chloride:cyclohexane; 60 mL of methylene chloride; and 20 mL of a mixture of 10% benzene, 20% methyl alcohol and 70% methylene chloride. The non-o,o'-Cl-substituted congeners were recovered by elution in the reverse flow direction with 50 mL of toluene. The toluene was concentrated by rotary evaporation and the solution was then transferred to 10.0 mL-screw-capped tubes and aliquots were analyzed by capillary GC-ECD.

Reagents: Solvents used were nanograde from Burdick and Jackson, Muskegon, MI. Glass fiber filters (Toyo GA200), used to make carbon/glass fiber sorbent (23), were purchased from Nuclepore Corp., Pleasanton, CA. Amoco PX-21 activated carbon was a gift of the Amoco Research Corp. 200 E. Randolph Dr., P.O. Box 5910-A, Chicago, IL. Chlorobiphenyl congeners were purchased from Analabs Inc., 80 Republic Dr., North Haven, CT, and Ultra Scientific Inc., 1 Main St., Hope, RI. Ring-UL-^{14}C-3,3',4,4'-TCB (11.04 mCi/mM) was obtained from Pathfinder Laboratories Inc., 11542 Fort Mims Dr., St. Louis, MO.

Instrumental and Data Processing: Details of analytical instrumentation and data processing for congener specific PCB analysis have been previously described (30). A Varian Model 3700

gas chromatograph equipped with a ^{63}Ni-ECD was used for analysis of cleaned-up samples. Data sampling and GC program operations were controlled by a Varian Autosampler Model 8000, which also delivered a calibrated amount of sample to the GC injection port. The isomer specific GC-ECD conditions for non-o,o'-Cl substituted PCBs were similar for all sample analyses: initial temperature, 170°C, programmed at 5°C/min to a final temperature of 240°C and held for 10 min; detector temperature, 300°C; and injector temperature, 220°C. The non-o,o'-Cl PCB congeners were separated with a glass capillary chromatographic column (30 m x 0.25 mm i.d.) coated with C_{87} stationary phase (Quadrex Corp., New Haven, CT). Hydrogen, with a linear velocity of 32 cm/sec, was used as the carrier gas, and nitrogen was delivered at 17 mL/min as the ECD makeup gas.

The method for congener specific total PCB analysis (including the mono-o,o'-2,3,3',4,4'-PeCB) differed from the procedure for non-o,o'-Cl chlorobiphenyls. However, the chromatographic conditions for congener specific analysis were similar for all samples: initial temperature 70°C, programmed at 1°/min to a final temperature of 250°C. Injector and detector temperatures were 220°C and 300°C, respectively. The o,o'-Cl substituted PCB congeners were separated by using a fused silica capillary column (60 m x 0.25 mm) coated with Durabond DB-5 (J&W Scientific, Inc., Rancho Cordova, CA); a 60-cm uncoated fused silica retention gap connected the GC injector to the analytical column. Hydrogen (linear velocity, 42 cm/sec) was used as the carrier gas and nitrogen as the detector make-up gas.

An IBM 9000 microcomputer interfaced with the GC acquired data generated by the electron capture detector. The data were pre-processed by a capillary applications program designed for laboratory data collection (IBM Instrument Division, Danbury, CT). The data were organized into a series of files on hard disk media using a Basic computer program and transferred off-line to a PDP-11/34 minicomputer (Digital Equipment Corp.).

Tree-structured disk files were formed using our specialized laboratory data base management computer programs written in DMS-11 (Digital Standard MUMPS, Digital Equipment Corp.) for the PDP-11 family of computers. We selected 105 congeners of PCB for quantitation and effected calibration by using Aroclors 1242, 1248, 1254, and 1260 in a 1:1:1:1 (w/w/w/w) mixture. The method of peak identification was a retention index system in which n-alkyl trichloroacetates were used (31). Molar response factors were determined from a flame ionization detector by using computer-based calculations (30). The response factors were then normalized to octachloronaphthalene, which served as an internal standard. After the concentrations of individual congeners were determined, the data were retrieved from the MUMPS-based laboratory data base and then transferred to an IBM-AT (IBM Corporation, Boca Raton, FL) microcomputer by way of an RS-232 link, using the computer program Cyber (Department of Linguistics, University of Illinois at Champaign-Urbana, Urbana, IL).

GC/MS Confirmatory Analysis: A Finnigan 4023 GC/MS acquired electron ionization mass spectra (35-510 d/sec). The capillary GC column was a 30 m x 0.25 mm DB-5 (0.25 μm). The temperature program was 60°C (1 min hold) to 210°C at 10°C/min, then to 290°C at 5°C/min. A mixed standard of the non-o,o'-Cl PCBs and a mixture of four Aroclors were analyzed along with the environmental samples. The GC/MS confirmatory analysis was done on the non-o,o'-Cl PeCB fractions of samples S422 and F142.

Principal Components Analysis: For data evaluation by Principal Components Analysis (PCA), we used SIMCA-3B (Soft Independent Modeling of Class Analogy) for MS-DOS based microcomputers (Principal Data Components, Columbia, MD). The concentration data obtained for each GC peak in each sample analysis were then expressed as fractional parts of the total and normalized to a sum equal to 100. Normalization minimizes the influence of total concentration and permits a comparison of compositional similarities among samples. The normalized data were examined by calculating the principal components sample scores T and variable loading terms P. After calculating three principal components for a class model, we prepared plots of sample similarity using the sample scores (T_1 vs T_2). The similarity of samples within the class can be assessed by the proximity of samples to each other in plots derived from principal components models. The statistical technique of cross-validation was used to determine the number of principal components that were statistically significant (32). Details of these procedures have been described elsewhere (33-36).

RESULTS AND DISCUSSION

High resolution GC with a DB-5 capillary column permitted the separation of more than 100 chlorobiphenyls from a 1:1:1:1 mixture of Aroclors 1242, 1248, 1254, and 1260, a number similar to that obtained by Mullin et al. (4). However, high resolution capillary analysis may not always adequately separate mono- and non-o,o'-Cl PCBs from other congeners, even with plate values (n) greater than 100,000. Fused silica SE-54 capillary GC columns have been used to resolve all but 11 pairs of PCB congeners in Aroclor mixtures (4). More recently Mullin (37) used fused silica DB-5 capillary GC columns for congener separations and was apparently successful in resolving 3,3',4,4'-TCB and 2,3,3',4,4'-PeCB from other PCBs. No 3,3',4,4'5-PeCB was detected in Aroclor mixtures using this direct analysis method. We found that direct capillary GC analysis of cleaned-up environmental PCB residues was adequate for 2,3,3',4,4'-PeCB but was generally inadequate for non-o,o'-Cl PCBs because of their low concentrations relative to those of other congeners. The advancements in capillary GC have not eliminated the need for selective enrichment of non-o,o'-Cl PCB congeners from PCB residues prior to GC analysis, as the highest concentrations of individual coplanar chlorobiphenyls ($\geq Cl_4$) in Aroclors appear to be less than 0.65% (w/w) of the PCB technical mixtures analyzed.

Only activated carbon and Florisil have been found suitable for the separation and enrichment of non-o,o'-Cl PCB congeners from bulk PCBs and environmental samples (18,19,38). Activated carbon adsorbents offer at least six advantages over Florisil: 1) high sample capacity with low sorbent mass (200 mg of Aroclor or gram quantities of lipid can be chromatographed on one gram of carbon); 2) activation or hydration differences due to variations in lots do not appear to affect carbon elution profiles of coplanar halogenated aromatics; 3) columns of carbon/glass fiber sorbent (23) and probably other types of carbon columns (20,21) are reusable, as more than 30 samples containing large amounts of lipids have been processed on one column with no apparent diminution of performance; 4) a lower ECD detection limit of non-o,o'-Cl chlorobiphenyls ($>Cl_3$) in Aroclor mixtures (approximately 0.4 µg/g of a PCB mixture); 5) greater selectivity as 95% of o,o'-Cl substituted PCB congeners are resolved from coplanar non-o,o'-Cl chlorobiphenyls with Florisil columns (38) and 99.3% with carbon columns (18); and 6) dispersed carbon columns have been routinely used as an

integral part of a semi-automated sequential chromatographic scheme for persistent halogenated contaminants (29).

The recoveries of non-o,o'-Cl substituted PCBs using the described methods for fish and sediments and the overall recovery of Aroclor 1248 from fish and sediment spikes, excluding the non-o,o'-Cl separations step, are shown in Table 2. Table 3 summarizes published data from the literature on the percentage (concentration of selected congener divided by total congener concentration) of 3,3',4,4'-TCB, 3,3',4,4'5-PeCB, and 2,3,3',4,4'-PeCB in technical Aroclor, Clophen and Kanechlor mixtures. The relatively small variance in the percentage of 3,3',4,4'-TCB detected in the listed Aroclors by different methods is surprising. Albro et al. (2) indicated that significant quantitative lot-to-lot and brand-to-brand variations exist in the congener composition of PCB mixtures. However, considerable differences were observed in literature values for 3,3',4,4'5-PeCB, and 2,3,3',4,4'-PeCB in technical PCB mixtures. Direct GC-ECD analysis of 2,3,3',4,4'-PeCB in Aroclor standards used in this study revealed the following contents: 1242, 0.43%; 1248, 1.5%; 1254, 3.1%; and 1260, none detected.

Table 2. Recoveries of selected non-o,o'-Cl substituted PCBs isolated by carbon/glass fiber chromatography

QC Sample Identification	Congener or Mixture Spiked	Amount Added (μg)	Non-o,o'-Cl PCB Recovery %
F147\1	1248	200	111
	^{14}C-3,3',4,4'	1.16	
F147	1248	200	97.6
	^{14}C-3,3',4,4'	1.16	
Reference\2 Soil	1248	100	117
	^{14}C-3,3',4,4'	1.16	
Reference Soil	1248	100	102
	^{14}C-3,3',4,4'	1.16	
Fish Solvent Blank	3,3'4,4'	0.98	
	3,3',4,4',5	1.38	131 (total)
	3,3',4,4',5,5'	0.78	
Soil Solvent Blank	3,3'4,4'	0.93	
	3,3',4,4',5	1.38	113 (total)
	3,3',4,4',5,5'	0.78	

\1 Yellow perch composite, contained 11.2 μg/g total PCB

\2 Topsoil sampled from the grounds of NFCRC

Table 3. Review of the literature on the percent content of 3,3',4,4'-TCB, 3,3'4,4',5-PeCB and 2,3,3',4,4'-PeCB in commercial PCB mixtures

Sample Type	3,3',4,4'-TCB % ± S.D. (replicates)	3,3',4,4',5-PeCB % ± S.D. (replicates)	2,3,3',4,4'-PeCB % ± S.D. (replicates)	Method (References)
Aroclors				
1016	ND\1	ND	NM\2	Carbon,
1242	0.24 ± .02 (3)	< 0.025 (3)	NM	C_{87} capillary
1248	0.34 ± .03 (5)	< 0.025 (3)	NM	GC-ECD (18)
1254	0.02 ± .001 (3)	< 0.025 (3)	NM	
1260	ND	< 0.025	NM	
Aroclors				
1242	0.23	NM	NM	Florisil,
1248				C_{87} capillary
FDA	0.24	NM		and OV-101
Allen	0.33	NM	NM	packed column
1254	ND	NM	NM	GC-ECD & MS
1260	ND	NM	NM	(38)
Aroclors			NM	
1242	0.35	ND	0.31	DB-5
1248	0.65	ND	1.11	capillary
1254	0.11	ND	2.71	GC-ECD
1260	0.11	ND	0.03	(37)
Aroclors				
1248	0.47	ND	< 0.01	charcoal,
1254	0.12	0.16	< 0.01	Dexil 410
1260	0.04	1.59	< 0.01	capillary
				GC-ECD
				(2)
Clophen				
A30	0.3	ND	0.5	SE-54
A40	0.7	ND	1.5	capillary
A50	1.1	ND	0.7	GC-ECD & MS
A60	ND	ND	0.2	(64)
Aroclors				
1242	0.52 ± 0.02	0.002 ± 0.000	NM	Carbon,
1248	0.61 ± 0.03	0.006 ± 0.000	NM	OV-1701
1254	0.06 ± 0.001	0.005 ± 0.000	NM	capillary
1260	0.06 ± 0.001	0.001 ± 0.000	NM	GC-ECD & MS\3
Kanechlor				(19)
300	0.44 ± 0.008	0.002 ± 0.000	NM	
400	0.85 ± 0.007	0.006 ± 0.000	NM	
500	0.15 ± 0.001	0.005 ± 0.000	NM	
600	0.07 ± 0.001	0.001 ± 0.000	NM	

\1 ND = None detected

\2 NM = Not measured

\3 Separate analyses were performed using OV-101 capillary columns with ECD and the residue values were confirmed by GC-MS

We chose to measure 3,3',4,4'-TCB residue because of its known presence in fish and invertebrates (18,22,39) and 3,3'4,4',5-PeCB because it is the most potent AHH inducer of the chlorobiphenyls (10). The mono-o,o'-Cl 2,3,3',4,4'-PeCB was also included with the non-o,o'-Cl congeners in these analyses because of its relatively high AHH induction potency and its high concentration in some Aroclor mixtures (Table 3), resulting in the potential for high TCDD-like activity in environmental samples. One investigator (19) has detected

3,3',4,4',5,5'- hexachlorobiphenyl in PCB technical mixtures (<1.2 μg/g), so we included it in our analyses.

To examine the fate of the mono- and selected non-o,o'-Cl substituted PCBs in an aquatic ecosystem, it is useful to have an approximation of the type, ratio, and congener specific composition of the original Aroclor mixtures released into the system of interest. This information can be used as a template to compare with PCB congener specific data of environmental samples, permitting an estimate of similarities and differences in congener composition due to the effects of environmental transport and transformation processes. Sample similarities or differences were determined with qualitative PCA which was performed at levels I and II as defined by Albano et al. (34).

Dunn et al. (40) has shown that partial least squares (PLS) in latent variables is a suitable PCA method for determining the ratio of Aroclor mixtures in samples resulting from the combination of several technical Aroclor mixtures. However, Schwartz et al. (41) and Stalling and Schwartz (42) showed that before PLS can be applied to environmental samples, they must pass the criterion of reasonable similarity to an Aroclor or mixtures of Aroclors. We stopped at level II PCA analyses in this study because the criterion of reasonable similarity (41,42) was not met by some fish and sediment samples.

The variance explained by the PCA model used in this study totaled 81%; 60% was explained by the first principle component, 12 % by the second, and 9 % by the third. A plot of sample scores (Theta-1 vs Theta-2) derived from the first and second principal components are shown in Figure 1. The "A" represents Aroclors, "F" fish samples, and "S" sediment samples. The SS and FF points in the plot represent overlapping values of sediment or fish. The residue profiles in the fish and sediment samples mediated clustering near or along a line intersecting Aroclors 1242 and 1248. The exception was F145, which appeared to be closely related to Aroclor 1254. To further explore the similarity of these samples to a mixture of Aroclor 1242 and 1248, a third principal component was used in Figure 2a. This plot shows that most of the fish and sediment samples were shifted in space perpendicular to a line intersecting Aroclors 1242 and 1248, it is also apparent that Aroclor 1260 lies on the side of the plane opposite that of the fish samples. Fish and sediment sample clusters in Figures 1 and 2a are not well separated because of the effect of S422. However, clustering of fish and sediment samples is distinct when S422 is removed from the class model (Figure 2b). Sample (S422) is unusual as IUPAC 4 (2,2') is the most concentrated congener, IUPAC 8 plus 5 (2,4';2,3) and 19 (2,2',6) are elevated, and the tetrachlorobiphenyls appear to be reduced relative to other samples (Figure 3). Examination of the variable plots corresponding to Figure 2a and 2b indicate that the high levels of IUPAC 4,5,8 and 19 in sample S422 were not responsible for its impact on the model. Based on the fugacity modeling of Burkhard (43) IUPAC 5,8 and 19 should be depleted in the sediment phase.

The recent work of Brown et al. (44) suggested that the atypical congener pattern observed in S422 (Figure 3) may be the result of reductive dechlorination by anaerobic bacteria. The elevated levels of 2,2' 4,4' (IUPAC 47) and 2,2',6 in S422 is consistent with the reported congener dechlorination patterns, but 3,3',4,4'-TCB was only slightly reduced (0.2% in S422 vs 0.24% and 0.34% for 1242 and 1248 mixtures [18], respectively). These results do not appear to follow Brown's et al. (44) predicted 50 to 100% decline of 3,3',4,4'-TCB. As Figure 2a and 2b show, the loci of fish and sediment sample data are

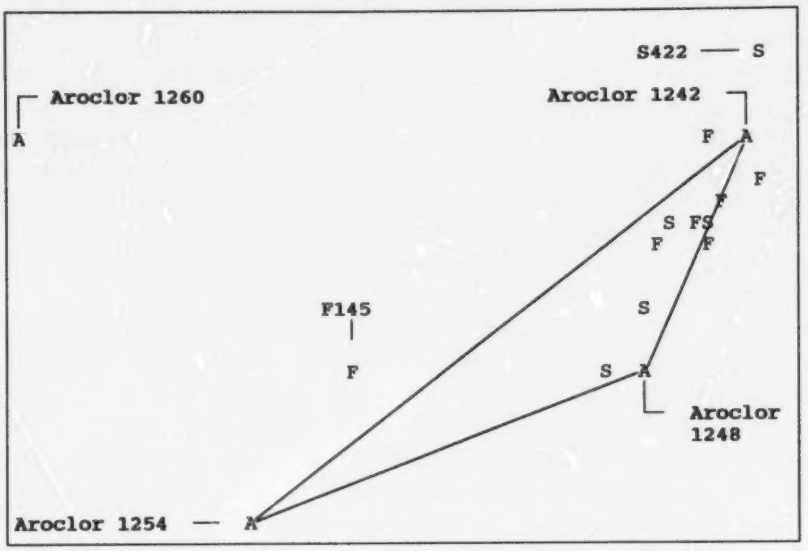

Figure 1. Principal components plot derived from the analysis of Aroclors, fish, and sediment samples. The letter "A" represents Aroclor standards; "F", fish samples; and "S", sediment samples. Both sediment and fish samples (note F145 is an exception) are located along a line intersecting Aroclor 1242 and 1248 standards.

above a line representing linear mixtures of 1242 and 1248. However, level II PCA classification results indicate that these samples can no longer be described in terms of Aroclors. This is not surprising because of significant differences in environmental distribution coefficients (Koc, BCF, and H) of PCB congeners and their degradation potentials (Table 4 and reference 44). Since the presence of linear combinations of Aroclors 1242 and 1248 is consistent with probable past PCB use in Waukegan Harbor (45), it appears that the PCB congeners in sediment and fish samples are weathered combinations of these Aroclors. Assuming that the congener specific data presented in Table 3 for Aroclor 1242 and 1248 are reflective of the original Aroclors entering Waukegan Harbor (e.g., no changes in congener composition or ratios during use), comparisons can be made between the percentage content of the selected mono- and non-o,o'-Cl congeners in standard mixtures of 1242 and 1248 and the percentage of the same congeners (relative to total PCB concentration) in sediment and fish samples. However, because principal components illustrate only spatial similarities and differences between environmental samples and Aroclors, difference histograms were used to examine the quantitative nature of these changes.

The histograms of the normalized concentration data in Figure 4 illustrate congener differences among a mixture of two technical Aroclors (25% 1242 plus 75% 1248) and representative samples of fish (F142) and sediment (S423). Some of the visual difference between these fish and sediment samples lies in the presence of IUPAC 17, peak #11, and 88, peak #40 in fish and its apparent absence in sediment. In addition, the following congener peaks were much higher in the sediment than in the fish: IUPAC 6, peak #4, 5 & 8, peak #5, 19, peak #6, 32, peak #13, 26, peak #15, 53, peak #20, and 51, peak #21. IUPAC 105, peak #67

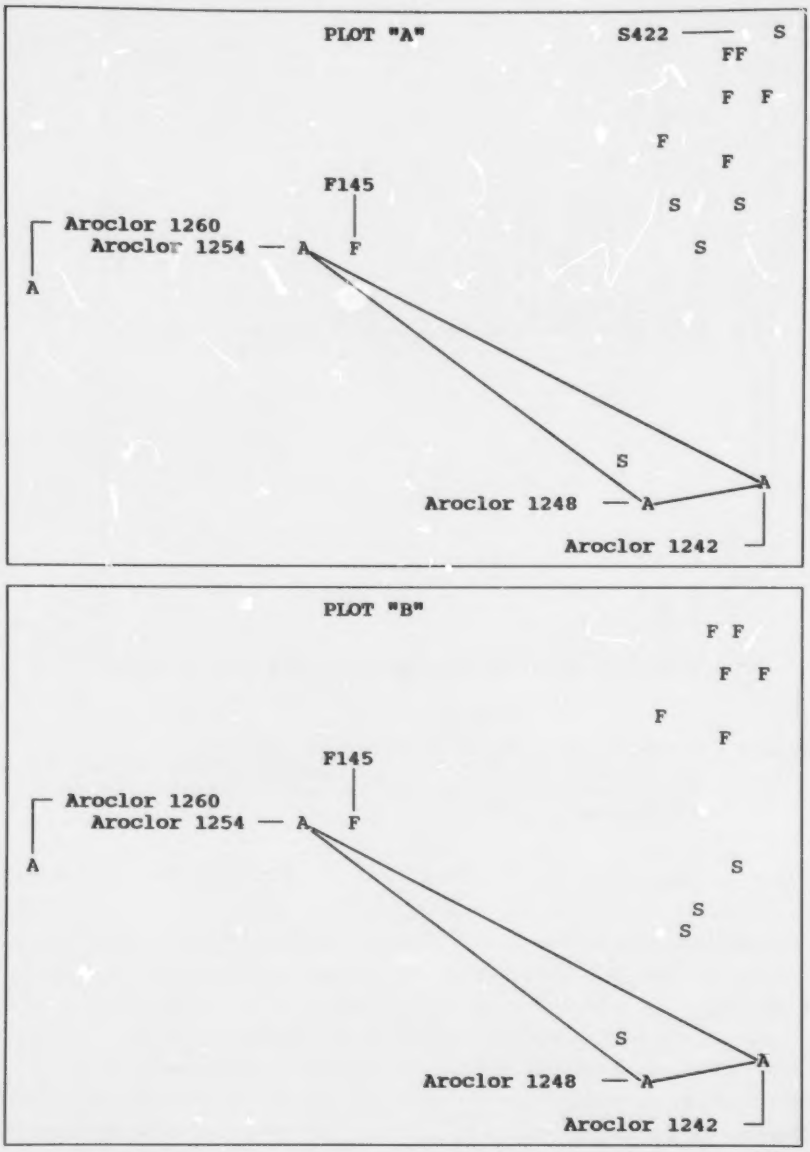

Figure 2 a,b. Principal components plots of the first and third components derived from the analysis of Aroclor, fish and sediment samples. The letters A, F and S represent Aroclors, fish and sediment samples, respectively. Plot "a" illustrates that fish and sediment samples (note F145 is an exception) are located in space directly above mixtures of Aroclors 1242 and 1248. Plot "b" shows improved separation and clustering of fish and sediment samples after removal of S422 (upper right corner of 2a) from the model.

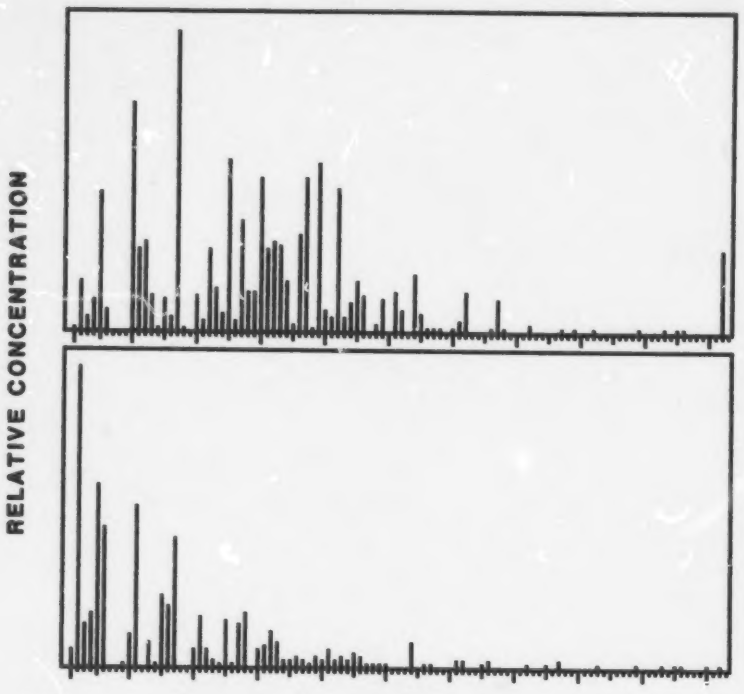

Figure 3. Concentration histograms of an Aroclor 1242/1248 1:3 (w:w) mixture (top) and an S422 (bottom) Waukegan Harbor sediment sample. Note the greatly reduced levels of more chlorinated PCB congeners in S422.

was slightly higher in the sediment sample than in the fish, whereas it was somewhat depleted in the fish relative to the mixture of Aroclors 1242 and 1248 (Figure 4). Other differences between the representative fish sample and the Aroclor mixture consisted of elevated amounts in the fish of IUPAC 17, peak #11, 26, peak #15, 25, #16 and reduced amounts of IUPAC 18, peak #10, 70 & 76, peak #37 and 56 & 60, peak #42. IUPAC 77 (3,3',4,4'-TCB) was not detected in the samples shown in Figure 4 because it requires carbon enrichment before GC analysis.

Figures 5 and 6 show representative capillary GC-ECD traces of the non-o,o'-Cl substituted PCB fractions after carbon enrichment of fish (F142) and sediment (S422) extracts from Waukegan Harbor. These samples contained 56.6 μg/g (fish) and 515 μg/g (sediment) of total PCB isomers prior to enrichment of non-o,o'-Cl PCBs with carbon/glass fiber columns. Tables 5 and 6 summarize the results of residue analyses for total PCb, 2,3,3',4,4'-PeCB and non-o,o'-Cl substituted PCB congeners in fish and sediment samples from Waukegan Harbor. Total PCB congener residues in fish ranged from 2.4 to 56.6 μg/g and averaged 33.4 ±19.8 μg/g (Table 5). Only 3,3'4,4'-TCB (non-o,o'-Cl PCB fraction) was detected in these samples by GC-ECD. The 3,3',4,4'-TCB concentrations in fish ranged from 2 ng/g to 89 ng/g in whole body tissue and averaged 45.3 ± 35.7 ng/g. The percentage (concentration of selected congener divided by total congener concentration) of 3,3',4,4'-TCB in PCB residues of fish samples averaged 0.133 ± 0.05 and varied only by 3.5-fold, whereas total PCB concentration varied

Table 4. Comparison of some physicochemical and biological properties of selected PCB congeners

Structure	IUPAC No.	H_2O Solubility µg/L (References)	Log Kows (References)	BCF\1 (References)	Koc\2	H\3
2,2',5,5'	52	26.5 (65)	6.26 (66)	33,700	60,600	2.5×10^{-3}
3,3',4,4'	77	0.6 (54) 17.4 (66)	5.81 (67) ± .049	15,300 4950-8600 (17)	34,500	9.4×10^{-3}
2,3,3',4,4'	105	4.0\4	6.29\5	35,500	62,900	7.6×10^{-4}

\1 BCFs not referenced were calculated by using the regression equation log BCF = 0.76 log Kow - 0.23 (68) based on 84 organic compounds exposed to fathead minnows, bluegill sunfish, rainbow trout, and mosquitofish; measured values based on rainbow trout (17)

\2 Koc values were calculated from the regression equation log Koc = .544 log Kow + 1.377 (68), based on a large number of organics including Aroclor 1254

\3 Values given are atm. m^3/mol. and were calculated by H = Pvp/S where Pvp is vapor pressure in atm. and S is water solubility in mol./m^3, vapor pressure values were from Bidleman (69)

\4 Water solubility was calculated from the regression equation log S = -1.49 log Kow + 7.46 (68)

\5 This value was derived from Burkhard's (43) molecular surface area equation: log Kow = 0.027147 (TSA) - 0.996029

23.6-fold. Normalization of the total PCB concentration to lipid content in fish increased the variability 5-fold instead of reducing it. This observation suggested that PCB residues in fish were not at equilibrium with the ambient environment. Residue heterogeneity in sediment and fish mobility may have been major factors in this apparent non-equilibrium status. All the fish samples contained 2,3,3',4,4'-PeCB which averaged 229 ± 160 ng/g. The mean percentage of 2,3,3',4,4'-PeCB relative to total PCBs in fish samples was 0.847 ± 0.52.

Residues of total PCBs in sediments varied by more than three orders of magnitude (Table 6). The percentage (same as defined for fish) of 3,3',4,4'-TCB in PCB residues of sediment samples varied by 1.4 orders of magnitude and averaged 0.16 ± 0.15. Residues of 3,3',4,4'-TCB ranged from 13 ng/g to 27,500 ng/g. The percentage of 2,3,3',4,4'-PeCB in PCB residues of sediments averaged 0.66 ± 0.37 and varied less than 3,3',4,4'-TCB.

Comparison of the percentage of 3,3',4,4'-TCB and 2,3,3',4,4'-PeCB in fish and sediment residues in this study with the percentage of 3,3',4,4'-TCB and 2,3,3',4,4'-PeCB in technical Aroclor mixtures suggested that the non-o,o'-Cl substituted congener may have been depleted in fish and sediment phases, whereas the mono-o,o'-Cl substituted congener was unchanged or within the percentile range of possible mixtures of Aroclors 1242 and 1248. These data appear to be consistent with the environmental partitioning of PCB isomers predicted by Burkhard (43). However, the significance of this type of comparison is currently unclear

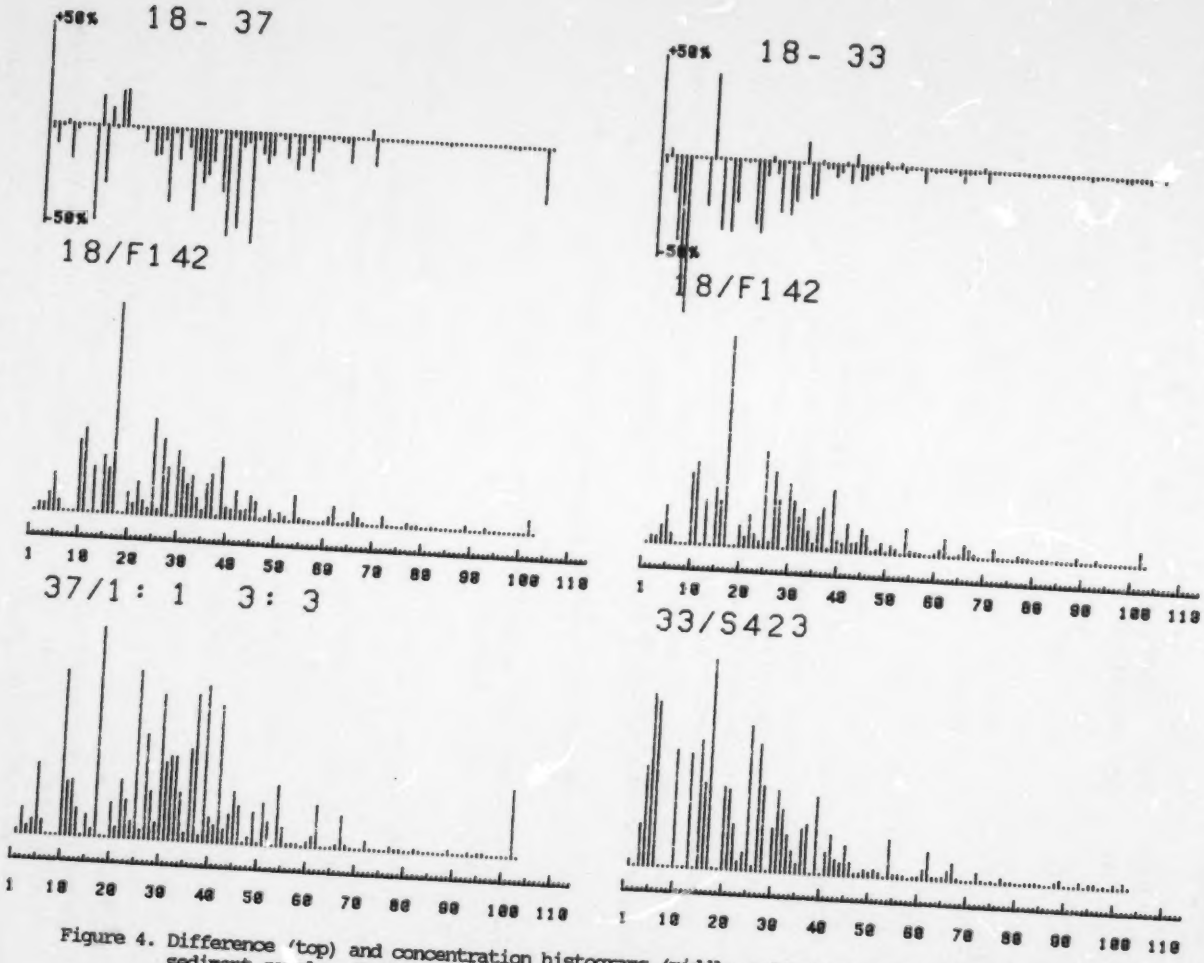

Figure 4. Difference (top) and concentration histograms (middle and bottom) from analysis of fish and sediment samples (left), and sediment and Aroclor 1242/1248, a 1:3 (w:w) mixture (right).

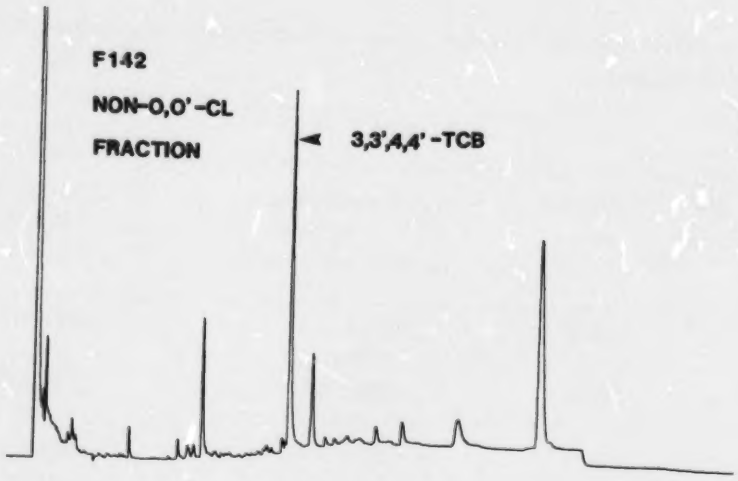

Figure 5. Capillary (C_{87}) EC chromatogram of the non-o,o'-Cl PCB fraction of a cleaned-up extract from largemouth bass offal.

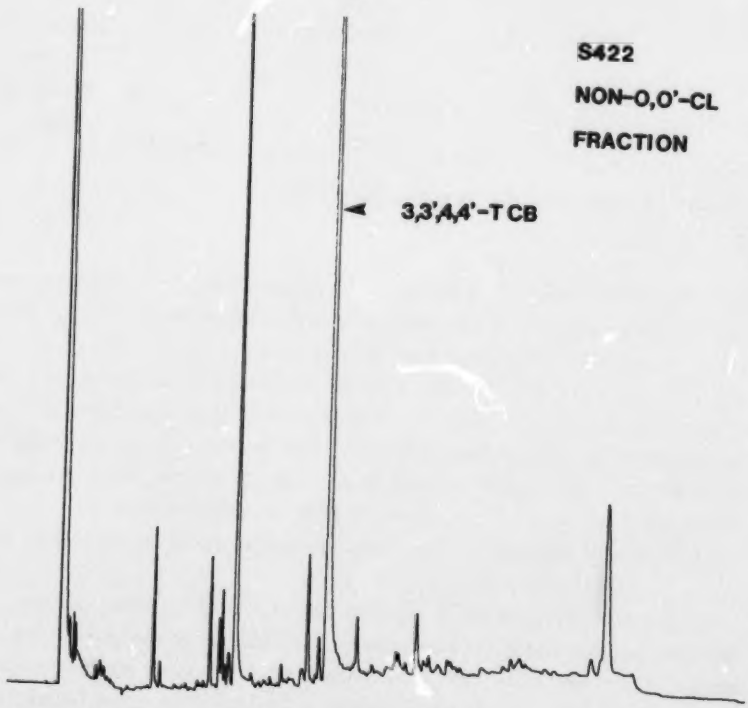

Figure 6. Capillary (C_{87}) EC chromatogram of the non-o,o'-Cl PCB fraction of a cleaned-up extract from a Waukegan Harbor sediment sample.

Table 5. Analysis of 2,3,3',4,4'-PeCB and non-o,o'-Cl substituted PCBs in fish from Waukegan Harbor of Lake Michigan\1

GC Column		DB 5	C_{87}	DB 5
Sample Identification	% Lipid	Total PCB µg/g	3,3',4,4'-TCB µg/g, % of Total (TCDD equivalents)\2	2,3,3',4,4',-PeCB µg/g, % of Total (TCDD equivalents)
F141	3	49.4	0.089, 0.18, (240)	.352, 0.71, (388)
F142	1	56.6	0.086, 0.15, (232)	.290, 0.51, (319)
F143	2	32.2	0.043, 0.13, (116)	.114, 0.35, (125)
F144	10	41.4	0.050, 0.12, (135)	.483, 1.17, (531)
F145	5	2.4	0.002, 0.08, (5)	.045, 1.88, (50)
F146	1	40.3	0.024, 0.06, (65)	.242, 0.60, (266)
F147	7	11.2	0.023, 0.21, (62)	0.080, 0.71, (88)

\1 3,3',4,4',5-PeCB and 3,3',4,4',5,5'-HCB were not detected
\2 Reported in pg/g

because of the difference demonstrated by SIMCA analysis between congener ratios representing these samples and those characteristic of the Aroclor mixtures believed to be the source of contamination. Still, the relative consistency of the percentage content of 3,3',4,4'-TCB and 2,3,3',4,4'-PeCB in the PCB residues of the fish samples examined, suggests that use of the mean of these percentile values on a site specific basis would permit the estimation of the concentration of these toxic isomers when only total PCB residue values are available.

The non-o,o'-Cl PCB fractions of F142 (Figure 5) and S422 (Figure 6) were analyzed by GC-MS. The presence of 3,3',4,4'-TCB was confirmed in both of these samples and 3,3',4,4',5-PeCB was tentatively detected in the sediment sample (S422) at very near its detection limit.

Since PCB residues did not appear to be at equilibrium in the study area, carbon normalization of sediment samples did little to reduced variability of residues. The heterogeneity of sample values may arise from direct input of waste PCB liquids into aquatic environments through turbulent advective events, resulting in hot spots of non-dissolved PCBs coating benthic sediments or liquid PCB globules of different geometric forms in contact with sediments. Equilibration with the larger environment is preceded by aqueous dissolution or direct sediment adsorption. Thibodeaux (46) developed several models to estimate benthic

Table 6. Analysis of 2,3,3',4,4'-PeCB and non-o,o'-Cl substituted PCBs in sediment from Waukegan Harbor of Lake Michigan[1]

GC Column	DB 5	C_{87}	DB 5
Sample Identification	Total PCB µg/g	3,3',4,4'-TCB µg/g, % of Total	2,3,3',4,4',-PeCB µg/g, % of Total
S421	6,996[2]	27.5, 0.39	43.4, 0.62
S422	515	1.05, 0.20	.352, 0.07
S423	126	.013, 0.01	.856, 0.68
S424	13,360	18.8, 0.14	131.0, 0.98
S425	10.6[3]	.005, 0.05	.102, 0.96

[1] 3,3',4,4',5-PeCB and 3,3',4,4',5,5'-HCB were not detected
[2] Mean of two determinations
[3] Mean of three determination

dissolution rates and the lifetimes of immiscible dense liquids in various geometric forms and environmental conditions. However, no laboratory or field data were found in the literature on the subject. PCB liquid dissolution and equilibration with the surrounding environment may be a relatively slow process that depends on liquid surficial area relative to PCB volume, volumetric water flow rate at the PCB liquid interface, and temperature. Factors other than PCB liquid dissolution rate which may affect the bioconcentration of PCBs include residue diffusion in sediment (intraparticle and interparticle) (47,48) and organism mobility and avoidance.

Conner (49) proposed the use of fish-sediment concentration ratios for chlorinated or polynuclear aromatic hydrocarbon (PAHs) contaminants, and suggested that the use of the resulting ratio may be more appropriate for risk assessment than bioconcentration factors (BCF) based on water column residues. This appears to be a good approach to use for PAHs in organisms having mixed-function oxygenase activity because high PAH metabolism and depuration rates result in lower than predicted BCFs (49). The fish-sediment ratio approach is also applicable to PCBs in aquatic ecosystems at equilibrium. However, its utility in ecosystems with highly heterogeneous (non-equilibrium) sediment residues is limited. The fish-sediment ratios in this study ranged from 1.78×10^{-4} to 5.34.

The environmental significance of AHH-inducing PCB residues is difficult to interpret because they are always present in organisms with many other PCB congeners and other classes of contaminants. Assessment of the toxicity of PCB congeners, which are isosteric to TCDD, has been simplified by using the "TCDD equivalents" approach (14,15). The AHH induction potency of each congener is determined and normalized against that of TCDD. The resulting

conversion factors are then multiplied by the appropriate environmental concentration (pg/g) of the congener selected to generate TCDD equivalent values. Total TCDD equivalents resulting from the addition of values of only the selected mono-and non-o,o'-Cl congeners present in fish samples (Table 5) ranged from 54.9 to 666 pg/g. The validity of the TCDD equivalents approach and the assumption of additivity was reviewed by Kubiak et al. (14). Bannister and Safe (50) have found that Aroclor 1254 was antagonistic to AHH and EROD induction by TCDD. However, potential antagonism by other PCB congeners and contaminant classes may only reduce but not eliminate the toxicity of AHH active PCB congeners. Nonadditive or synergistic effects have been observed (52) in male Wistar rats resulting from submaximal (induction response) exposures to 2,3',4,4',5,5'-hexachlorobiphenyl in conjunction with non-o,o'-Cl PCBs. Obviously, additional research is needed to fully validate the "TCDD equivalents" approach.

Information on the environmental persistence of the AHH-inducing PCB congeners examined in this study is generally limited to the 3,3',4,4'-TCB congener. Furukawa et al. (53) found that the pseudo-first order degradation rate constant for 3,3'4,4'-TCB was too slow to measure in a lake water column and sediment. However, the work of Brown et al. (44) suggested that PCBs buried in anoxic benthic sediments are subject to reductive dechlorination by anaerobic bacteria. Two major questions need to be addressed in regard to the reductive dechlorination process: What are the rate constants for the degradation of the toxic PCB congeners? What mass fraction of Great Lakes PCBs are being acted on by this anaerobic process? Burkhard (43) predicted that 3,3',4,4'-TCB and several other non-o,o'Cl PCBs of an equimolar congener mixture would be enriched in the water phase and depleted in the air phase based on their Kocs and Henry's law constants. If Burkhard's model is correct for Aroclor mixtures, a significant amount of the AHH-inducing PCB mass may be in Great Lakes water columns and not subject to anaerobic degradation. In this work, 3,3',4,4'-TCB appears to be somewhat reduced in sediment and fish when compared to its concentration in the hypothesized original Aroclor mixture.

Physicochemical properties of 3,3',4,4'-TCB (used as a representative of non-o,o'-Cl PCBs) differ from those of other ortho-substituted PCB isomers. Recently, the water solubility of 3,3',4,4'-TCB was determined to be 0.57 μg/L (54), which is low relative to that of other tetrachlorobiphenyl isomers (6 to 170 μg/L) and is one-fifth that of the smallest calculated value (derived from congener Kow or TSA). The vapor pressure of 3,3',4,4'-TCB (1.6×10^{-5} mm Hg) is also the lowest and the melting point (180°C) the highest of the tetrachlorobiphenyl isomers (55,56). The relative aquatic volatility of an organic compound (not miscible with water) can be estimated by its Henry's law constant, which is a function of pure liquid vapor pressure and water solubility. Based on the above vapor pressure and water solubility values, a Henry's law constant of 9.4×10^{-3} atm. m^3/moles was derived by the following relationship: H = Pvp/S, where Pvp is vapor pressure in atm, and S is water solubility in moles/m^3 (Table 4). This relatively high value implies rapid volatilization from water columns (mass transfer controlled by liquid phase), and probably differs significantly from Burkhard's prediction due to the much lower water solubility value (54) we used in calculating the Henry's constant. However, because most of the AHH-inducing PCB isomers (especially the non-o,o'-Cl substituted) can assume a nearly planar configuration, potentially enhancing sorption, partitioning onto organic and mineral surfaces

may retard volatilization from aquatic environments. Unpublished data from our laboratory suggests that less that 20% of 3,3',4,4'-TCB was lost after 1 week through volatilization from mass balance microcosms (57) containing only water, whereas >75% of 2,2',5,5'-TCB was volatilized under similar conditions. Sorption on glass surfaces and a slow dissolution rate appeared to play a major role in the relatively low volatility of 3,3',4,4'-TCB.

Shaw and Connell (58) suggested that PCB congener potential for coplanarity is a major factor in the bioconcentration of chlorobiphenyls. They found a strong inverse relationship between increasing o,o'-Cl substitution of PCB congeners and BCFs in polychaetes and mullet (84-day static exposures). This correlation was ascribed to increased molecular surface area available for tissue interaction in the case of isomers with decreasing o,o'-Cl substitution. Kannon et al. (59) found that uptake and depuration rates of coplanar PCB congeners from mussels exposed to PCBs in Hong Kong waters were much slower than ortho-substituted congeners. The first order half-lifes of 3,3',4,4'-TCB in mussels was 9.3 days, whereas other isomers (≥Cl number) were two days or less. Opperhuizen and Voors (60) observed slow depuration rates of 3,3',4,4'-TCB from female guppies relative to 2,4,5-trichlorobiphenyl. Using their data, the calculated first order half-life ($t_{\frac{1}{2}} = .693/k_2$, where k_2 = depuration rate constant) for 3,3',4,4'-TCB was 34.6 days, whereas $t_{\frac{1}{2}}$ for 2,3,5-trichlorobiphenyl was only 2.5 days. Mizutani et al. (61) speculated that in mice the observed increase in half-lives of hexachlorobiphenyl isomers with decreasing o,o'-Cl substitution was due to slower release rates from lipid rather than metabolism. However, Niimi and Oliver (62) found that rainbow trout depuration of PCB isomers (single oral dose) was enhanced within an isomer group (eg. Cl_4) by decreasing o,o'-Cl substitution and vicinal unsubstituted (Cl) carbon atoms.

Stalling et al. (17) reported moderate BCFs (4950 to 8600) for rainbow trout exposed to non-o,o'-Cl 3,3',4,4'-TCB (50-day flow-through water exposure), but a greater half-life than 2 through 4 o,o'-Cl substituted congeners in Aroclor 1248. Several mono-o,o'-Cl PCBs (including 2,3,3',4,4'-PeCB) had the highest BCFs in rainbow trout of the congeners in 1248. In this study the percentage content of 2,3,3',4,4'-PeCB in PCB fish residues did not appear to be depleted relative to that of the Aroclor mixtures (1242 plus 1248) suspected to be the source of contamination. The observed reduction of 3,3',4,4'-TCB in fish PCB residues relative to mixtures of 1242 and 1248 does not necessarily confirm low BCFs for non-o,o'-Cl PCBs because of the lack of water concentration data and the apparent non-equilibrium status of PCBs in the study area.

CONCLUSIONS

A method for the analysis of non-o,o'-Cl PCBs and the most AHH active mono-o,o'-Cl PCB in environmental samples was described. Direct ECD analysis of cleaned-up extracts with capillary DB-5 GC columns was satisfactory for quantifying 2,3,3',4,4'-PeCB, which represented more than 1% of the total congener mass in Aroclors 1248 and 1254. However, the AHH active non-o,o'-Cl PCBs required carbon enrichment prior to capillary GC analysis. Both 2,3,3',4,4'-PeCB and 3,3',4,4'-TCB were detected in all the fish and sediment samples analyzed. The percentage of 3,3',4,4'-TCB and 2,3,3',4,4'-PeCB in PCB residues of fish samples appeared to be reduced in the case of 3,3',4,4'-TCB and about the same for

2,3,3',4,4'-PeCB, when compared with the percentage contents of the same analytes in the Aroclor mixtures suspected to be the source of PCB contamination in Waukegan Harbor (45).

TCDD equivalents, based on 2,3,3',4,4'-PeCB and 3,3',4,4'-TCB residues, reached a high of 666 pg/g in a whole body white sucker composite sample. Because of the potential for complex organochlorine residues in organisms to elicit non-additive responses, further research is required to validate the TCDD equivalents approach.

Predicting the environmental distribution of non-o,o'-Cl PCBs is problematic, because of differences in experimental results and calculated values reported in the literature, and the general lack of physicochemical measurements on these toxic compounds. The low volatilization rate of the 3,3',4,4'-TCB from aquatic microcosms (57) may be due to the following: 1) higher than predicted (calculated from Kow or TSA) sorption coefficient, 2) desorption hysteresis, 3) slow aqueous dissolution rate, and 4) lower vapor pressure or higher water solubility than reported.

The elevated levels of di- and trichlorobiphenyls relative to tetra- and pentachlorobiphenyls in one sediment sample (S422) suggest that anaerobic reductive dechlorination (44) had occurred, as this peak pattern would not be expected to result from simple partitioning. However, we observed very little reduction of 3,3',4,4'-TCB in this sediment sample (S422) when compared to its relative concentration in Aroclor 1242 or 1248 (18). Brown et al. (44) indicated that 3,3',4,4'-TCB and 2,3,3',4,4'-PeCB, as well as other PCB congeners having chlorine atoms in the 4,4' positions, were preferentially reduced by anaerobic dechlorination in sediments. This is in contrast to findings (5,63) that recalcitrant PCBs in fish and birds have chlorines substituted in the 4,4'-position.

Improved assessment of the environmental distribution and persistence of toxic AHH-inducing PCB congeners is dependent on the experimental determination of their anaerobic degradation rate constants (sediments), desorption isotherms from sediments, aqueous dissolution rates and BCFs in aquatic organisms. Current data are not adequate to confidently predict the aquatic fate of AHH inducing PCB congeners.

SIMCA analyses in this and earlier studies (41,42) have shown that PCB congener ratios in fish and sediment samples differ from each other and from Aroclor mixtures. Still needed are SIMCA analyses of mass balance microcosm data of Aroclor congener partitioning between sediment, water, air and biota phases. Results of these analyses may permit determination of the source and types of Aroclor mixtures originally released into the environment and the specific changes in congener peak profiles representative of temporal and spatial dissipation of PCBs in the simulated aquatic ecosystem.

ACKNOWLEDGMENT

We thank Ginger Gibson for her technical assistance and Dave Stalling for some SIMCA analyses and histogram generation. We are also grateful for the GC-MS analysis of selected samples by Paul Peterman and the helpful comments of Tim Kubiak.

REFERENCES

1. Zell, M., H.J. Neu, K. Ballschmiter, Z. Fresenius (1978), Anal. Chem. 292, 97.
2. Albro, P.W., J.T. Corbett, and J.L. Schroeder (1981), J. Chromatogr. 205, 103.
3. Ballschmiter, K., and M. Zell, Z. Fresenius (1980), Anal. Chem. 302, 20.

4. Mullin, M.D., C.M. Pochini, S. McCrindle, M. Romkes, S.H. Safe and L.M. Safe (1984), Environ. Sci. Technol. 18, 6.
5. Ballschmiter, K., M. Zell, and H.J. Neu (1987), Chemosphere 7, 173.
6. Safe, S. (1987), Chemosphere. 16, No. 4, 791.
7. Kubiak, T.J., H.J. Harris and J. Trick (1985), Microcontaminants and Reproductive Impairment of Forster's Tern on Green Bay. Final Report. Sea Grant Office, ES0105, Univ. of Wisc.-Green Bay, Green, WI.
8. Tanabe, S. (1988), Environ. Pollut. 50, 5.
9. Trotter, W.J., S.J. Young, J.L. Casterline, Jr., J.A. Bradlaw, and L.R. Kamops (1982), J. Assoc. Off. Anal. Chem. 838, 65.
10. Sawyer, T. and S. Safe (1982), Toxicol. Ltrs. 13, 87.
11. Goldstein, J.A. (1980), In: "Halogenated Biphenyls, Terphenyls, Naphthalenes, Dibenzodioxins, and Related Compounds", Kimbrough, R. D., Ed,: Elsevier/North Holland: New York, Chapter 6, 151.
12. Parkinson, A. and S. Safe (1981), Toxicol. Environ. Chem. Rev. 4, 1.
13. Yoshimura, H., S. Yoskihara, N. Koga, K. Nagata, I. Wada, J. Kuroki, and Y. Hokama (1985), In: "Environmental Health Perspectives," U. S. Dept. of Health and Human Services, Publication no. (NIH) 85-218, Feb. 59, 113.
14. Smith, L.M., T.R. Schwartz and T.J. Kubiak (1986), Occurrence of AHH-Active Polychlorinated Biphenyls, Dibenzodioxins, and Dibenzofurans in Lake Michigan Sediment and Biota. The Question of Their Relative Toxicological Significance. Extended Abstract Presented Before the Division of Environmental Chemistry, American Chemical Society, Sept. 7-12.
15. Kannan, N., S. Tanabe and R. Tatsukawa, Bull. Environ. Contam. Toxicol (In press).
16. Mayer, F.L., P.M. Mehrle and H.O. Sanders (1977), Arch. Environ. Contam. and Toxicol. 5, 501.
17. Stalling, D.L., J.N. Huckins, J.D. Petty, J.L. Johnson and H.O. Sanders (1979), In: "Annals of the New York Academy of Sciences: Health Effects of Halogenated Aromatic Hydrocarbons", Edited by W. J. Nicholson and J. A. Moore 320, 48.
18. Huckins, J.N., D.L. Stalling and J.D. Petty (1980), J. Assoc. Off. Anal. Chem. 63, No. 4, 750.
19. Kannan, N., S. Tanabe, T. Wakimoto and R. Tatsukawa (1987), J. Assoc. Off. Anal. Chem. 70, No. 3, 451.
20. Kannan, N., S. Tanabe, T. Wakimoto and R. Tatsukawa (1987), Chemosphere 16, No. 819, 1631.
21. Tanabe, S., N. Kannan, An. Subramanian, S. Watanabe and P. Tatsukawa (1987), Environ. Pollut. 47, 147.
22. Stalling, D.L., J.N. Huckins and J.D. Petty (1980), In: "Hydrocarbons and Halogenated Hydrocarbons in the Aquatic Environment", Edited by B.K. Afghan and D. Mackay, 131.
23. Smith, L.M. (1981), Anal. Chem. 53, 2152.
24. Neely, W.B. (1983), In: "Physical Behavior of PCBs in the Great Lakes", Edited by D. Mackey, S. Paterson, S.J. Eisenreich and M.S. Simmons. Ann Arbor Science, 71.
25. Rapaport, R.A., and S.J. Eisenreich (1984), Environ. Sci. Technol. 18, No. 3, 163.
26. Stalling, D.L., R.C. Tindle (1972), J. Assoc. Off. Anal. Chem. 55, 32.
27. Schwartz, T.R., R.G. Lehmann (1982), Bull. Environ. Contam. Toxicol. 28, 723.
28. Schmitt, C.J., J.L. Zajicek and M.A. Ribick (1985), Arch. Environ. Contam. Toxicol. 14, 225.
29. Smith, L.M., D.L. Stalling and J.L. Johnson (1984), Anal. Chem. 56, 1830.
30. Schwartz, T.R., R.D. Campbell, D.L. Stalling, R.L. Little, J.D. Petty, J.W. Hogan, and E.M. Kaiser (1984), Anal. Chem. 56, 8, 1303.
31. Schwartz, T.R., J.D. Petty, and E.M. Kaiser (1983) Anal. Chem. 55, 1839.
32. Wold, S. (1978), Technometrics 20, 397.
33. Wold, S. and M. Sjostrom (1977), In: "Chemometrics, Theory and Application", Edited B.R. Kowalski, ACS Symposium Series No. 52. American Chemical Society. Washington, DC, 243.
34. Albano, C., W.J. Dunn III, U. Edlund, K. Esbensen, S. Hellberg, E. Johansson, W. Lindburg and M. Sjostrom (1978), Anal. Chem. Acta. Comput. Tech. 103, 429.
35. Wold, S. (1982), Kemia-Kemi 9, 401.
36. Wold, S., C. Albano, W.J. Dunn III, U. Edlund, P. Geladi, S. Hellberg, E. Johansson, W. Lindberg and M. Sjostrom (1984), In: "Chemometrics, Mathematics and Statistics in Chemistry", D. Reidel Publishing Co., Dordrecht, Holland 17.
37. Mullin, M.D., Chairman (1985), Congener Specific, PCB Analysis Techniques Workshop, EPA Large Lakes Research Station, Gross Ils, MI, June 11-14. 38 p.
38. Kamops, L.R., W.J. Trotter, S.J. Yound, A.C. Smith, J.A.G. Roach and S.W. Page (1979), Bull. Environ. Contam. Toxicol. 23, 51.

39. Bush, B., K.W. Simpson, L. Shane, and R.R. Koblinzt (1985), Bull. Environ. Contam. Toxicol. 34, 96.
40. Dunn, W.J., D.L. Stalling, T.R. Schwartz, J.W. Hogan, J.D. Petty, E. Johansson and S. Wold (1984), Anal. Chem. 56, No. 8, 1308.
41. Schwartz, T.R., D.L. Stalling and C.L. Rice (1987), Environ. Sci. Technol. 21, 72.
42. Stalling, D.L., and T.R. Schwartz, "Classification of Polychlorinated Biphenyl Residues: Isomers VS Homologue Concentrations in Modeling Aroclors and Polychlorinated Biphenyl Residues," Anal. Chem., In Press.
43. Burkhard, L.P., D.E. Armstrong and A.W. Andren (1985), Chemosphere. 14, Nos. 11/12, 1703.
44. Brown, J.F. Jr, L. Bedard, M.J. Brennan, J.C. Carnahan, H. Feng and R.E. Wagner (1987), Science 236, 709.
45. Armstrong, D.E. (1980), "Sediment sampling, water sampling and PCB analysis in Lake Michigan", Final Report on Project No. 2-800-03-218-03, to JRB Associates, Inc., Mclean, VA.
46. Thibodeaux, L.J. (1979), Chemodynamics: Environmental Movement of Chemicals in Air, Water and Soil. John Wiley and Sons, New York, NY, 501P.
47. Karickhoff, S.W. (1980), In: "Contaminants and Sediments, Volume 2, Analysis, Chemistry and Biology", Edited by R.A. Baker, Ann Arbor Science Publishers, 193.
48. Fisher, J.B., R.L. Petty and W. Lick (1983), Environ. Pollut. (Series B), 5, 121.
49. Conner, M.S. (1984), Environ. Sci. Technol. 18, 1, 31.
50. Bannister, R. and S. Safe (1987), In: The Toxicologist, Abstracts of the Annual Meeting, 7, No. 1, 160.
51. Keys, B., J. Piskorska-Pliszczynska and S. Safe (1986), Toxicol. Ltrs. 31, 151.
52. Leece, B., M. A. Denomme, R. Tourner, A. Li and J. Landers (1987), Con. J. Physiol. Pharmocol. 65, 1908.
53. Furukawa, K., K. Tonomura and A. Kamibayashi (1978), Appl. Environ. Technol. 35, 223.
54. Dickhut, R.M., A.W. Andren and D.E. Armstrong (1986), Environ. Sci. Technol. 20, No. 8, 807.
55. Foreman, W.T. and T.F. Bidleman (1985), J. Chromatogr. 330, 203.
56. Hutzinger, O., S. Safe, and V. Zitko (1974), The Chemistry of PCBs. CRC Press, Cleveland, OH, 269 p.
57. Huckins, J.N. (1987) Unpublished Research Results, NFCRC, U.S.F&WS.
58. Shaw, G.R. and D.W. Connell (1984), Environ. Sci. Technol. 18, 18.
59. Kannan, N., S. Tanabe, R. Tatsukawa and D.J.H. Phillips, Environ. Pollut. Submitted for publication.
60. A. Opperhuizen and P. Voors (1980), Chemosphere, 16, Nos. 10-12, 2379.
61. Mizutani, T., K. Hidaka, T. Ohe, M. Matsumoto, K. Yanamoto, and K. Sojima (1980), Bull. Environ. Contam. Toxicol. 25, 181.
62. Niimi, A.J., and B.G. Oliver (1983), Can. J. Fish. Aquat. Sci. 40, 1388.
63. Bush. B., C.F. Tumasonis, and F.D. Baker (1974), Arch. Environ. Contam. Toxicol. 2, No. 3, 195.
64. Duinker, J.C. and M.T.J. Hilebrand (1983), Environ. Sci. Technol. 17, 449
65. Hague, R. and D. Schmedding (1975), Bull. Environ. Contam. Toxicol. 14, 13.
66. Bruggeman, W.A., V.D. Steen and O. Hutzinger (1982), J. Chromatogr. 238, 335.
67. Burkhard, L.P. and D.W. Kuehl, Chemosphere (1986), 15, No. 2, 163.
68. Bysshe, S.E. (1982), In: "Handbook of Chemical Property Estimation Methods, Environmental Behavior of Organic Compounds", Edited by W.J. Lyman, W.F. Reehl and D.H. Rosenblatt. McGraw Hill Book Company, p 4-8 & 5-4.
69. Bidleman, T.F. (1984), Anal. Chem. 56, 2490.

(Received in Germany 5 July 1988; accepted 2 August 1988)

NOTICE

This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

This article documents research that was conducted under the auspices of the U.S. Environmental Protection Agency (USEPA). As an arm of the government, the USEPA has a paid up, non-exclusive, irrevocable, worldwide license to reproduce, prepare derivative works, and distribute to the public all of the material contained herein, and to grant others acting on its behalf the right to do so. The USEPA grants to the National Technical Information Service, Department of Commerce, the right to act as its agent in the distribution of this material.